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(54) CHEMICAL PRODUCT DRYING METHOD

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, Missouri 63166, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved method for drying trichloro-s-triazine trione.

Trichloro-s-triazine trione, sometimes termed trichloroisocyanuric acid or trichlorocyanuric acid, is a well known material which is widely employed as a source of available chlorine in sanitizing and bleaching applications. It is used, for example, in various cleaning and bleaching formulations and is also a well known substitute for elemental chlorine in swimming pools.

It is known to prepare trichloro-s-triazine trione by several different methods. One typical method is described in U.S. Patent No. 2,969,360. In this process, cyanuric acid is fed along with aqueous alkali (in molar ratio of about one mole of caustic per atom of chlorine to be added) and chlorine to an aqueous reaction zone which is maintained at a pH in the vicinity of 3.5. The crude trichloro-s-triazine trione precipitates from the solution as a solid slurry. The slurry product is continually or periodically filtered to separate the crystalline products from the mother liquor whereupon the crystalline product is dried.

Prior art processes for producing trichloro-s-triazine trione have been beset with numerous difficulties. For example, considerable manufacturing downtime and rate variances have been experienced in the manufacture of trichloro-s-triazine trione because of difficulties in dewatering which result in a slushy feed to the dryer. When very wet or slushy product material reaches a conventional dryer such as a vibrating heated pan dryer, it frequently becomes necessary to reduce the production rate or shut down the unit to avoid packaging wet trichloro-s-triazine trione. Those skilled in the art recognize the undesirability of pack-

aging wet trichloro-s-triazine trione because of the evolution or gassing of chlorine and NCl_3 within the packaging drum. The latter condition is potentially hazardous and undesirable for other reasons.

It is known to employ fluid bed drying for trichloro-s-triazine trione although certain disadvantages can be encountered with this method. For example, dust generation presents a problem; the fluid bed can collapse when overheated; wet cake mixing with hot, drying material in the bed can produce hazardous NCl_3 , and the large mass of material within the fluid bed dryer can cause difficulties under certain operating conditions.

A phenomenon associated with the drying cycle of trichloro-s-triazine trione is the effect of maximum drying temperature on the eventual density of the dried particles. It has been observed, for example, that a less dense particle is obtained when the particle temperature during drying exceeds about 130°C ., as compared to the density of dried particles exposed to lower drying temperatures.

An abrupt absorption of heat into the particle is usually observed when the particle temperature during the drying step is allowed to exceed about 130°C .

The phenomenon associated with particle drying temperatures in excess of about 130°C . is sometimes referred to as a phase change. The reduced density of the particle obtained after cooling is characterized by expansion of the lattice in the crystalline structure of the particle.

Although the reduction in physical density is not in itself undesirable, there are certain characteristics of the "phase change" crystals which make those crystals less desirable than the normal crystals for many applications. For example, there is evidence that the phase change crystals or particles are more difficult to compact into tablets or other solid shapes. Particles which have gone through the phase change are found to exhibit poorer stability in some bleaching formulations. Such particles often exhibit unusual electrostatic properties which contributes to blending problems in subsequent granulation steps. In

manufacturing practice, the particle density of trichloro-s-triazine trione is used to determine which phase particle is present, i.e., the normal phase or the high temperature phase.

Two key objectives in the drying of trichloro-s-triazine trione, therefore, are to maintain the particle temperature during the drying step at such a level as to avoid the high temperature phase change and to avoid excessive moisture in the dried product to obviate the tendency toward storage drum gassing. Less than about 0.25% by weight moisture in the dried product is usually acceptable for trichloro-s-triazine trione.

Trichloro-s-triazine trione, with its absorption of heat during phase change coupled with latent expansion of the crystal lattice structure, is clearly seen to behave differently from the alkali metal dichloro-s-triazine triones which also are used in sanitizing, bleaching and chlorine-supplying applications. It is well known that the alkali metal dichloro-s-triazine triones, when exposed to a high temperature source, can begin to burn and continue burning after the initial heat source has been removed until all of the material is consumed. Heat is naturally given off during this occurrence. This phenomenon is referred to as self-sustaining and self-propagating decomposition. Because of this diverse behaviour between the acid and the salts, provisions for drying the respective materials are substantially different and essentially unrelated. Prior art teachings applicable to the handling and drying of alkali metal dichloro-s-triazine triones are therefore not necessarily valuable in finding improved drying methods for trichloro-s-triazine trione. We have now found that by airstream flash drying (sometimes called pneumatic conveying-type drying) of wet trichloro-s-triazine trione avoids many of the difficulties previously experienced in the drying of trichloro-s-triazine trione.

The method of the invention for drying wet trichloro-s-triazine trione particles comprises introducing the particles into a gas stream flash dryer and controlling the particle temperature between 80°C. and 120°C.

The method of the invention permits the feeding of product wet cake (filter cake or centrifuge cake) directly to the dryer without having previously divided or beaten the wet cake into discrete particles such as in the method of U.S. Patent No. 3,289,312. In the method of the invention, the dust problems experienced with certain prior art methods of drying trichloro-s-triazine trione are reduced.

In practicing the present invention, trichloro-s-triazine trione wet cake or centrifuge cake may be prepared by any of several conventional methods such as hereinbefore described. The wet, solid product is separated

from the reaction medium or slurry and may thereupon be directly used in the drying method of this invention. Surprisingly, it has been found unnecessary to employ recycled dried product in cooperation with the wet material for providing a feed to the airstream flash dryer. Thus, wet trichloro-s-triazine trione may be fed directly to the dryer without recycle of dried material, thereby avoiding the prior art hazard of NCl_3 development. Particle temperature should be controlled in a manner which minimizes or avoids the occurrence of high temperature phase change, and in accordance with the present invention, this is achieved by controlling the particle temperature in the gas stream flash dryer 80°C. and 120°C. Superior results have been achieved with particle temperature control between 95°C. and 105°C. which results in moisture content in the final product between 0.2% and 0.25% by weight. Such moisture levels have been found to be acceptable for most applications of trichloro-s-triazine trione. Excessive drum gassing is usually not encountered with trichloro-s-triazine trione product containing moisture levels within that range.

The duration of gas stream flash drying in the method of this invention varies according to the desired particle temperature which in turn is dependent upon hot gas temperature in the dryer stream. In pneumatic conveying dryers such as those which are useful for gas stream flash drying according to the present method, the heat transfer is by convection from the conveying gas. Moisture is almost instantaneously removed from wet solid particles by dispersing and conveying them in direct intimate contact with the hot gas. The characterizing feature of gas stream flash drying is the extremely short retention time which is typically from 3 to 10 seconds but may sometimes be even a fraction of a second.

With a free-flowing material and primarily surface moisture only, the dryer frequently assumes the form of an gas-conveying system using heated gas the conveying medium.

There are four fundamental factors which govern evaporation in a short retention time convection dryer (gas stream flash dryer) where the heat is supplied and the moisture transported by air or other gases. These factors are moisture dispersion, temperature differential, particle size and agitation. Such factors are described in detail and typical airstream flash dryers are illustrated on pages 242 to 251 of the *ENCYCLOPEDIA OF CHEMICAL PROCESS EQUIPMENT*, by William J. Mead, Reinhold publishing Corporation, New York, New York (1964).

In carrying out the method whereby wet trichloro-s-triazine trione is flash dried, air

is the preferred contacting medium although other drying gases may also be utilized to achieve the same result. In this regard, the contact of gas and solid may be carried out using any of the drying apparatus known to those skilled in the art which permits intimate contact of the product particles with the gas for the required time duration.

The typical particle temperature range recited herein for airstream flash drying of wet trichloro-s-triazine was established because at particle temperatures in the vicinity of 130°C., phase change coupled with crystalline lattice expansion upon cooling can occur which results in a reduction in particle density. Similarly, at particle temperatures below about 80°C., an undesirable increase in product moisture is usually encountered which, as described above, can lead to evolution of chlorine and NCl₃ (gassing) within the storage drums.

The method of the present invention is illustrated by Example 2 below. Example 1 describes a typical preparation of trichloro-s-triazine trione. Parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Although conducted on a laboratory scale, this process scheme for preparing trichloro-s-triazine trione is adaptable to continuous manufacturing operations. A feed solution was prepared by mixing a cyanuric acid slurry with sodium hydroxide to produce a solution containing 7.6% cyanuric acid with a mole ratio of sodium hydroxide to cyanuric acid of 3.2:1. The chlorination reaction was provided for by a jacketed 1.4 liter glass reactor equipped with a stirrer, side arm for product overflow, subsurface feed tube and a fritted glass sparger. Starting with water in the reactor, feed solution is introduced through the feed tube at about 40 ml./min. and chlorine is introduced through the sparger at about 5.5 grams/min. The pH was controlled in the range of 3.5 to 3.8 by adjusting the chlorine feed rate and reaction temperature was controlled between 22°C. and 27°C. by circulating ice water through the reactor jacket. The product slurry, which overflows the side arm, is filtered to separate the wet crystalline product from the mother liquor. Preliminary drying of the crystals to be flash dried was achieved by filtering on a fritted glass filter on a suction flask. The wet cake of trichloro-s-triazine trione thus prepared contained 8 percent moisture and when airdried had an air pycnometer density of 2.08 grams/ml. as measured by an air pycnometer.

EXAMPLE 2

This Example illustrates the direct conversion by airstream flash drying of wet

trichloro-s-triazine trione to a final product form containing less than 0.25% moisture. A full scale flash dryer of a design similar to that described in the *ENCYCLOPEDIA OF CHEMICAL PROCESS EQUIPMENT* was utilized in conjunction with a continuous manufacturing process adapted from the exemplary product preparation set forth in Example 1. The flash dryer was started up maintaining a vent temperature of 145°C. Centrifuged cake comprising wet trichloro-s-triazine trione from the continuous manufacturing process was fed directly to the dryer with no recycle of dried material. After startup of the airstream flash dryer the particle temperature and vent air (exit air) temperature of the dryer were gradually lowered until a maximum product density was reached with a product moisture of less than 0.25%. Density measurements were obtained with a conventional air pycnometer. Samples were taken from the discharge of the airstream flash dryer cyclone for moisture and density measurement after each change in dryer temperatures. This provided data relating product temperature, product moisture and stability. The product temperature was allowed to drop slightly below the optimum to determine the necessary control ranges and the moisture loss through the airveying and compaction system. Several natural upsets occurred during this process which demonstrated the system's ability to handle surges in feed flow rate and moisture content. Samples also were taken from the mill discharge and finished product at each dryer temperature to determine any effect of dryer conditions and product stability on the product cut obtained through compaction and screening efficiencies.

Particle temperature was conveniently controlled in the airstream flash dryer by adjusting the burner temperature. Particle temperature was measured in the dump gate at the discharge of the dryer cyclone. A direct relationship was found between particle temperature and product moisture in the final trichloro-s-triazine trione product. In a preferred embodiment of the present invention, a control range of about 100°C. to 105°C. in particle temperature afforded a desirable moisture level in the final product between 0.2 and 0.25%. It was surprisingly found that such careful control of particle temperature will preclude the production of "wet" material. If the specified particle drying temperatures are maintained, the trichloro-s-triazine trione product will be dried regardless of upset in the feed. In at least one instance the wet cake feed to the flash dryer became so wet that a portion was not airveyed but instead collected at the bottom of the dryer which resulted in a plugging condition that had to

be washed out. Notwithstanding the occurrence of this processing upset, no wet material was produced from the flash dryer during that time. No difficulties were encountered in feeding the centrifuged cake from the manufacturing process directly to the dryer. This condition prevailed even though previously dried material was not recycled to the dryer intake. This unexpected advantage was surprising in view of prior art difficulties encountered with attempts to process centrifuged cake or filtered cake directly to a drying apparatus. The dryer exhaust temperature necessary to maintain the particle temperature in the range of 100°C. to 105°C. was 135°C to 140°C. Inlet temperatures to the dryer were normally 220°C. to 240°C. depending on rate and feed moisture content. Depending upon the process equipment upstream of the dryer, significant variations can be expected in the line temperature control ranges.

A relationship was found which relates particle density values readable by air pycnometer at the airstream dryer discharge to phase change. Thus, it was observed that those particles having a pycnometer reading of about 2.02 grams per milliliter or higher as they exit from the dryer, will exhibit on aging (e.g., for 24 hours) the same density as particles which were air dried at room temperature. Such particles have obviously not undergone phase change. In contrast, however, particles which undergo phase change because of excessive drying temperatures usually exhibit pycnometer values of about 1.9 grams/ml. at the dryer discharge and, upon aging, never exceed about 2.00 grams/ml. pycnometer density values.

WHAT WE CLAIM IS:—

1. A method for drying wet trichloro-s-

triazine trione particles, which comprises introducing the particles into a gas stream flash dryer and controlling the particle temperature between 80°C. and 120°C.

2. A method according to Claim 1 wherein the particle temperature is controlled between 95°C. and 105°C.

3. A method according to either of Claims 1 and 2 wherein the wet particles introduced into the flash dryer are in the form of a wet cake taken from a filter or centrifuge.

4. A method according to any of Claims 1 to 3 wherein the retention time of the particles in the flash dryer is such that the dried trichloro-s-triazine trione has a moisture content not greater than 0.25 percent by weight.

5. A method according to any of Claims 1 to 4 wherein the gas stream flash dryer is an air stream flash dryer.

6. A method according to any of Claims 1 to 5 wherein the density of the freshly dried product at the dryer discharge is 2.02 grams/ml, or greater and the density after aging for at least 24 hours approaches 2.08 grams/ml.

7. A method according to Claim 3 wherein the wet cake has a moisture content not exceeding 12% by weight.

8. A method according to Claim 1 substantially as described in Example 2.

9. Trichloro-s-triazine that has been dried by a method according to any of Claims 1 to 8.

J. C. LUNT,
Chartered Patent Agent,
Monsanto House,
10—18 Victoria Street,
London, SW1H 0NQ.